Glass and Ceramics, Vol. 67, Nos. 11 – 12, March, 2011 (Russian Original, Nos. 11 – 12, November – December, 2010)

AT ENTERPRISES AND INSTITUTES

UDC 666.189.2:666.193

SOME ASPECTS OF THE MANUFACTURING PROCESS FOR OBTAINING CONTINUOUS BASALT FIBER

A. G. Novitskii[1, 2] and M. V. Efremov[1]

Translated from *Steklo i Keramika*, No. 11, pp. 30 – 34, November, 2010.

Some features of the mechanism of basalt melt glass formation are reported. The effect of the characteristics of the basalt melt on the quality of continuous fibers is demonstrated. The advantages of multioperator technology for production of continuous basalt fiber are substantiated.

Key words: basalt, melt, continuous fiber, technology, fiber quality.

Production of continuous basalt fiber is based on melting ground basalt in a founding aggregate followed by drawing filaments from the melt obtained. The fibers are spun through the holes in spinneret plates. Despite the variety of the physical processes that take place in the fiber spinning unit, melting of the basalt with production of a melt is determining.

Production of the basalt melt can be considered as a process of melting a heterogeneous system consisting of several physically homogeneous mineral silicate compounds which are in the form of crystals and glass. In overall appearance, the basalt melt is a dark glass melt, so that the theories and hypotheses of spinning a glass melt can be applied to processes of spinning a basalt melt.

Many hypotheses on the structure of glass have been advanced over the past 100 years. According to the crystallite hypothesis of A. A. Lebedev [1], the structure of glass is in the form of a skeleton of irregularly positioned atoms or ions constituting the basic mass of the glass and containing sections whose degree of ordering gradually increases, forming so-called crystallites. N. V. Belov [2] showed that there is an analogy (the type of bonds, coordination numbers of structural elements, etc.) in the structural relationship between the glass and the corresponding crystalline compounds. According to the structural-coordination hypothesis of Dittsel' and Appen [3], the properties of glass are primarily determined by the degree of coherence of the basic skeleton formed by the glass formers and the coordination state of modifier cations. According to the aggregate hypothesis of O. K. Botvinkin [4], chemical compounds or the ions constituting them are preserved in the structure of the glass and manifested on crystallization of the glass as crystals of defined composition. According to V. V. Tarasov [5], inorganic glasses have the structure of continuous branched skeletons consisting of chains formed by silicon-oxygen anions in the electric field of metal cations. Tarasov believes that these glasses differ from organic glasses only by the fact their skeleton (polymer) has the character of a polyvalent ion radical and the cations have the character of a monomer.

All of the hypotheses thus assume the presence of a high-polymer, aperiodic skeleton which is nevertheless not free of individual ordered microregions. This skeleton is formed by structural polyhedrons in the form of infinite anion radicals of the glass former in the electric force field of modifier cations.

The hypothesis concerning the crystallite structure of glass has undergone some changes between the time it was advanced and the present. The study of the structure of different glasses clearly shows the microheterogeneity of their structure. It follows that real glasses consist of the ordered part of crystallites and unordered amorphous matter. Most scientists agree that the structure of glass is amorphous-crystallite.

The following affect ordering of the structure of the melt: the melting temperature, the time the melt is held at temperatures above the crystallization temperature, the presence of alkali metals in the composition of the cations, the effect of an electromagnetic field, the presence of strong van der

[1] MINERAL 7 Co., Novyi Yar, L'vov Region, Ukraine.
[2] E-mail: raomineral@gmail.com.

Waals bonds. The presence of a "mineral memory" suggests that the bonds in the structure of glass are not as strong as in a crystalline body. This is confirmed by the lower chemical stability of glass in comparison to samples of the same crystal structure composition.

A study of glasses from basalt melt obtained in different temperature conditions showed that the chemical stability of the glass increased with a decrease in the cooling rate, while the strength decreased. The reverse dependence was obtained when the melt preparation temperature was increased. The dependence was preserved with an increase in the time of holding the melt at a certain temperature above the crystallization temperature. The electromagnetic treatment of the melt, which strengthens the effect of destruction of the "mineral memory" and produces high strength of the glass, is also an important factor that affects the properties of the glasses obtained. The possibility of restoring the structural mineralogical composition of a crystalline body from a melt with an intact "mineral memory" if cooling is conducted at a low rate and with holding at certain temperatures is also an important factor in working with glass from rocks. This points to partial confirmation of the crystallite hypothesis.

A basalt melt is formed in the temperature range from 1720 to 1535 K for an upper crystallization boundary temperature in the region of 1530 K. These temperatures are different for the different kinds of basalt raw material used for processing. In this respect, establishing the ranges of the temperature conditions is a basic element in controlling the manufacturing process of obtaining the melt and production of continuous basalt fiber with given properties.

Degassing, which consists of removing the gases in the melt, is an important stage in production of a high-quality melt. This process takes place in holding the melt at temperatures above 1720 K. The holding time is approximately 2 h. The viscosity of the melt is approximately 150 Pa · sec.

Spinning the fiber from the melt through spinnerets is determined by the viscosity of the glass and character of the change in it as a function of the temperature, upper crystallization boundary, the rate, and the surface tension. Basalt melts suitable for obtaining a continuous fiber must be characterized by a low crystallization rate [6]. If the tendency of the melt to crystallize is high, the process must be conducted at a higher temperature than the temperature corresponding to the required viscosity, which results in additional technical difficulties. If the glass has a low crystallization rate, then fibers can be spun from it, and if the processing temperature corresponds to the crystallization temperature or is even lower than this temperature.

Technologically, basalt glass should have a comparatively wide processing range, i.e., the temperature range in which the process properties of the glass, primarily the viscosity, have fixed values and are not subject to sharp changes. Basalt glass, which is characterized by a wide processing range, does not require careful regulation of the temperature and the production process is more stable. The difference between the final and initial processing temperatures must be approximately 100 K for a stable manufacturing process.

The effect of high temperatures on the glass-forming constituents modifies them, creates new bonds, and forms the structure of the glass. These factors significantly affect the characteristics of the melt. By varying the melting temperature range, the holding time of the melt in the high-temperature medium, and the conditions of cooling the melt during production of the continuous fiber, the quality of the final product can be effectively controlled.

In addition to the controllable temperature effect on the raw material, selection of the raw material itself is an important factor in production of high-quality fiber. The chemical composition of the raw material predetermines the temperature conditions of production of the melt, its characteristics, and in the final analysis, the quality of the product obtained [7].

As indicated above, The technology for mechanically drawing the filaments from the melt is the basis of production of continuous basalt fiber. This technology is now implemented by two methods which only differ in the equipment formulation. In the first method, small furnace aggregates of the modular type (modular technology) are used with the possibility of installing one to two slit spinneret feeders or plates in the furnace aggregate. In the second method, multioperator (multioperator technology) furnace aggregates with 6 to 12 jet and spinneret feeders are used. The basic manufacturers of continuous basalt fiber are developing production in these two directions. Some characteristics of basalt fiber manufactured by different manufacturers both with the modular and with the multioperator technology are reported in Table 1.

The modular technology is characterized by relatively small initial investments, the possibility of fast startup, and smooth increases in production capacities. In our opinion, the basic advantage is the possibility of successively putting the modular furnaces on line and stopping operation of each concrete furnace individually without significantly affecting the manufacturing process of the other furnaces and the production volumes. Startup and operation of the modular furnace aggregate takes 3 – 4 days.

The drawbacks of modular technology concern the comparatively low quality of the fiber obtained. This is due to the small area of the bath furnace, which significantly reduces the time the melt passes through the degassing and homogenization stage. The fiber obtained with this technology is not much better than the glass fiber made from E-glass. In addition, the amount of wastes with this technology is approximately 40%.

The main advantage of the multioperator technology is the stability of the manufacturing process for production of basalt fiber whose characteristics are close to the high-quality characteristics of fiber made from S-glass. This is primarily attained due to the significant size of the bath furnace, which ensures the maximum amorphousness of the melt due

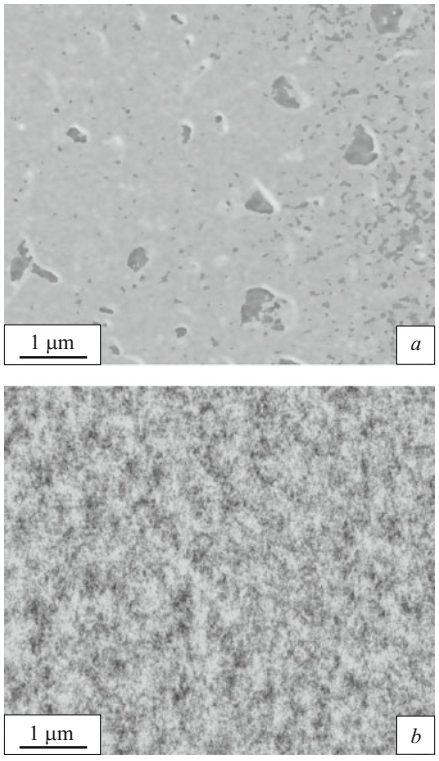

Fig. 1. Structure of basalt fiber glass before (*a*) and after (*b*) exposure of the melt to an electromagnetic field.

to the increase in the melt holding time at a certain temperature and the almost total elimination of crystals. In addition, the jet feeders used in the manufacturing process increase the plasticity of the melt, neutralizing the ion bonds of cations and anions by the electric field effect. The effect of the electromagnetic field on the structure of the glass by means of its action on the bonds between the individual formations constituting the melt is shown in Fig. 1. The glass without treatment of the melt with an electromagnetic field has large crystalline inclusions. After magnetic treatment of the melt, the size of the crystals in the same glass decreased significantly, and random distribution of the constituent elements appeared in the melt. It was found that the strength of the fiber obtained from such a melt was 20% higher than the strength of the fiber made from the untreated melt.

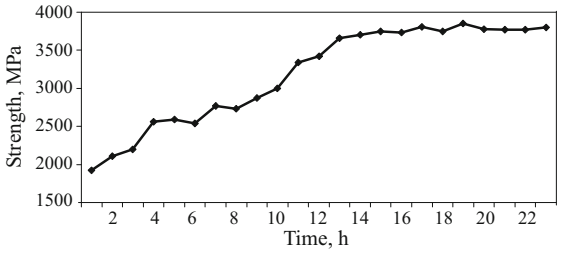

Fig. 2. Strength of basalt fiber as a function of holding the melt at 1720 K.

As a function of the manufacturing process, the time of passage of the basalt from loading into the furnace to processing of the fiber is from 14 to 18 h, which allows almost totally excluding (or significantly reducing) the effect of the "mineral memory" of the basalt on the fiber spinning process. The dependence (Fig. 2) of the strength of basalt fiber

TABLE 1. Characteristics of Basalt Fiber from the Basic Manufacturers

Manufacturer	Average strength of elementary basalt fiber, MPa		Tensile modulus of elasticity (Young's) of elementary fiber, GPa	Nonuniformity of diameter, μm
	Modular technology	multioperator technology		
Tekhnobazal't, Slavuta,* Ukraine	2100	–	76	17 ± 5
Ivotsteklo, Ivota,* Russia	2550	–	79	13 ± 4
NTB, Bucha,* Ukraine	2200	–	77	17 ± 5
Kompozit Plant, Serov,* Russia	1750	–	82	13 ± 3
Teploizolyatsiya, Belichi,* Ukraine	2100	3100	80	12 ± 3
Vulkan NPO Ltd., Osa, Russia	1850	–	79	13 ± 4
Secotech, Korea*	1800	–	77	17 ± 5
Chengdu Aerospace Tuoxim Science & Technology Co., Chengdu, China	1750	–	77	17 ± 6
Shanghai Russia Gold Basalt Fiber, Shanghai, China	1650	–	76	18 ± 7
Kamennyi Vek, Dubna,* Russia	–	3750	87	13 ± 2
Sudogda Glass Fiber Plant, Sudogda,* Russia	–	3400	82	12 ± 2
S-Glass Lanxi Joel Fiberglass Co., Ltd., China	4650	4650	89	18 ± 1
E-Glass Hengshui Yixing Fiberglass Co., Ltd., China	2050	2050	71	15 ± 2

* The fibers are manufactured from andesite basalt from the Transcarpathian Region (Ukraine).

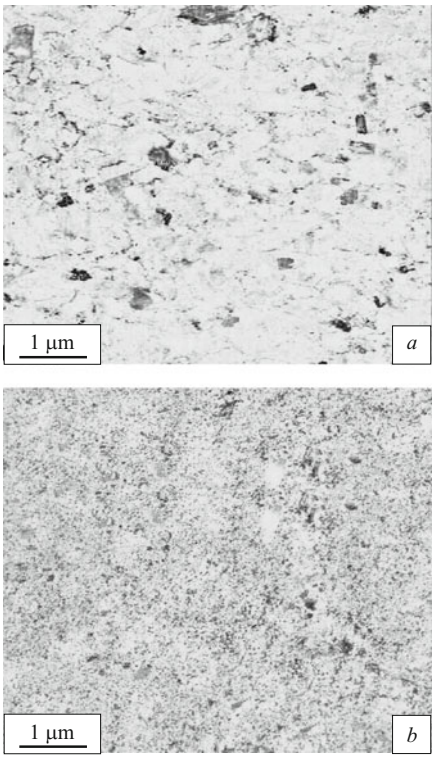

Fig. 3. Structure of glass from basalt melt after holding at 1720 K: *a*) holding for 2 h; *b*) holding for 14 h.

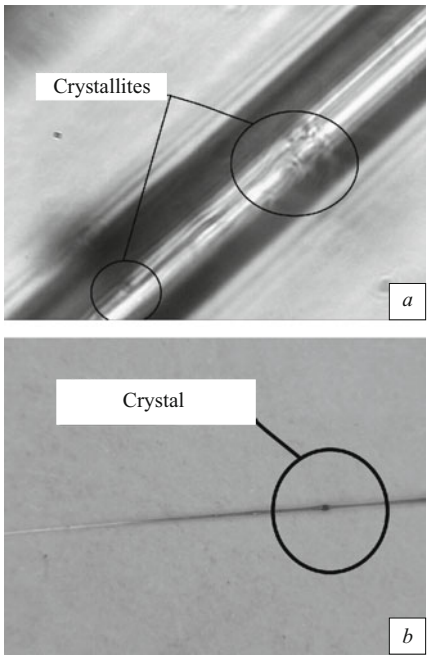

Fig. 4. Crystals and crystallites in continuous basalt fiber: *a*) crystallites; *b*) crystal.

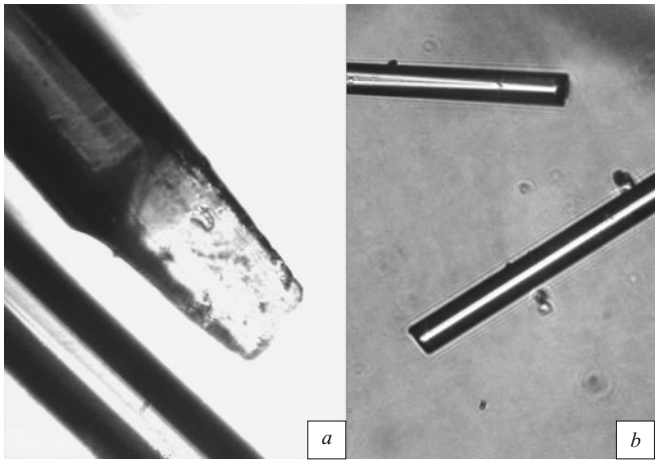

Fig. 5. Section of fiber: *a*) brief holding of melt; *b*) holding of melt for 14 h.

on the time the melt is held at 1720 K (the fiber strength was determined according to GOST 6943.10–79 with minor changes) was obtained with the results of the studies.

When the melt was held for 4 to 8 h at 1720 K, the magnetite and other ore minerals and tourmaline and mica dissolved. Quartz, pyroxene, etc. were more difficult to dissolve. Pyroxene decomposed into silica and olivine crystals. Olivine partially consists of forsterite, whose melting point is 2170 K, but it dissolves in time under the effect of the fluxes in the melt. The most intensive dissolution of crystals takes place for 14 h. The system then gradually passes into a state of equilibrium, confirmed by the relatively similar strength of the fiber obtained in holding the melt for 14 to 24 h. The structure of the glasses obtained at different holding times gives a graphic picture (Fig. 3). Large crystals which did not dissolve are clearly visible in the basalt glass with holding of the melt for 2 h at 1720 K. The particle size decreased significantly in the glass obtained from the melt held for 14 h.

The fibers made from the melt prepared by modular technology had both large crystals and crystallites (Fig. 4).

In studying the section of the fiber prepared with brief holding of the melt, we found that the section of the fiber had a multitude of different planes (Fig. 5*a*).

The section of the fiber obtained in holding the melt for more than 14 h had several planes (Fig. 5*b*), i.e., fracture takes place according to the fluctuation theory of the strength of glass [8]. This once more confirms the advantage of multioperator technology. Its next advantage is that the process of manufacturing continuous fibers with the corresponding equipment formulation and qualified servicing personnel takes place with almost no malfunctions. There are also no interruptions when the fiber processing units are replaced. The design of the furnace aggregate allows operating for three years without capital repairs of the lining. Startup and operation of the furnace aggregate takes approximately 7 days. The amount of wastes with this technology is less than 5%.

The results of the studies demonstrate the promise of developing production of continuous basalt fiber with multioperator technology, in contrast to the conclusions drawn by other investigators [9].

CONCLUSIONS

Despite the plethora of hypotheses concerning glass formation, many investigators agree that the structure of glass is amorphous-crystallite.

The effect of high temperatures and an electromagnetic field on the glass-forming constituents modifies them, creates new bonds, and forms the structure of the glass, which significantly affects the characteristics of the melt.

The quality of the final product can be effectively controlled by changing the melting temperature range, melt holding time at high temperatures, and the melt cooling conditions during production of continuous fiber.

The comparative analysis of the two methods of basalt fiber production showed that high-quality basalt fiber can only be obtained with the so-called multioperator technology.

REFERENCES

1. A. A. Lebedev, *Proceedings of the "Glass Structure" Conference* [in Russian], Izd. AN SSSR, Moscow – Leningrad (1955), pp. 360 – 362.
2. N. V. Belov, *Structure of Ion Crystals and Metal Phases* [in Russian], Moscow (1947).
3. Yu. M. But, G. N. Duderov, and M. A. Matveev, *General Silicate Technology* [in Russian], Gosstroiizdat, Moscow (1962).
4. O. K. Botvinkin, *The Glassy State* [in Russian], Izd. AN SSSR, Moscow – Leningrad (1965).
5. V. V. Tarasov, *Problems in the Physics of Glass* [in Russian], Gosstroiizdat, Moscow (1979).
6. A. G. Novitskii and M. V. Efremov, "Features of production of chemically stable, continuous basalt fiber," *Khim. Promisl. Ukr.,* No. 1 (2003).
7. A. G. Novitskii, "Basalt raw material. Selection technology for production of fibers for different applications," *Khim. Promisl. Ukr.*, No. 2 (2003).
8. G. M. Bartenev, *Structure and Mechanical Properties of Inorganic Glass. Glasses* [in Russian], Gosstoiizdat, Moscow (1966).
9. B. K. Gromkov, A. N. Trofimov, S. G. Chebryakov, and S. M. Oreshko, "Analytical review of development of continuous basalt fiber technology in Russia and Ukraine," *Glass Russia*, No. 8 (2009).